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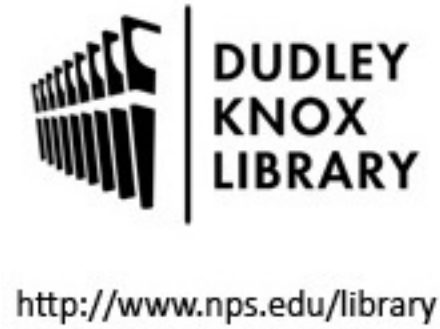

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MEASUREMENT OF THERMO-ELECTRIC POWER IN THE TEMPERATURE RANGE OF 80°K TO 230°K FOR GERMANIUM, LEAD TELLURIDE, AND BISMUTH TELLURIDE

JOSEPH F. YURSO

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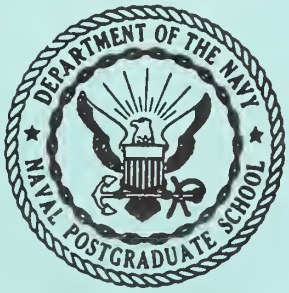

THESIS

MEASUREMENT OF THERMOELECTRIC POWER

IN THE TEMPERATURE RANGE OF 80°K to 230°K

FOR GERMANIUM, LEAD TELLURIDE, AND BISMUTH TELLURIDE

Joseph F. Yurso
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MEASUREMENT OF THERMOELECTRIC POWER IN THE TEMPERATURE RANGE OF 80°K TO 230°K FOR GERMANIUM, LEAD TELLURIDE, AND BISMUTH TELLURIDE

* * * * *

Joseph F. Yurso

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by

Joseph F. Yurso
Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
MECHANICAL ENGINEERING

United States Naval Postgraduate School
Monterey, California

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Joseph F. Yurso

This work is accepted as fulfilling
the thesis requirements for the degree of
MASTER OF SCIENCE
IN
MECHANICAL ENGINEERING
from the
United States Naval Postgraduate School

ABSTRACT

An apparatus for measuring the thermoelectric power in the temperature range of 80°K to 270°K is described. Measurements of thermoelectric power versus temperature in the above temperature range for samples of germanium, lead telluride, and bismuth telluride were performed. The general method of measurement is the determination of the thermoelectric power, $\frac{\Delta E}{\Delta T}$, where ΔE is the thermal emf measured between two points in the sample and ΔT is the temperature difference between these same two points determined through thermocouple readings.

The experimental work was performed at the U. S. Naval Postgraduate School, Monterey, California, during the winter and spring of 1960.

ACKNOWLEDGEMENTS

The writer expresses his appreciation to Professor C. E. Menneken and Professor P. F. Pucci for their advice and encouragement. Thanks are also due to Mr. Hollis Oren for his assistance in preparing the measuring apparatus.

The following companies very generously made samples available for measurements:

The Martin Co., Baltimore, Maryland - Lead telluride, p and n types

Texas Instruments, Dallas, Texas - Germanium, single crystal, p type

The assistance of the Bureau of Ships and the Naval Research Laboratory in obtaining thermoelectric materials and valuable information is greatly appreciated.

TABLE OF CONTENTS

Section	Title	Page
1.	Introduction	1
2.	Analysis of Problem and Experimental Techniques	12
3.	Results	17
4.	Conclusions	27
5.	Recommendations Concerning Future Work	29
6.	Bibliography	32
Appendix		
I	Material Properties	35
II	Experimental Errors	36
III	Data	38
IV	Sample Calculations	41
V	Photographs of Experimental Apparatus	42

LIST OF ILLUSTRATIONS

Figure		Page
1.	Thermoelectric Devices	5
2.	Figure of Merit Parameters versus Carrier Concentration	7
3.	Thermoelectric Power of Germanium	10
4.	Schematic Diagram for the Measurement of Thermoelectric Power	13
5.	Arrangement for Measurement of Thermal EMF	15
6.	Arrangement for Measurement of Thermal EMF	15
7.	Arrangement for Measurement of Thermal EMF	15
8.	Arrangement for Measurement of Thermal EMF	15
9.	Switching Arrangement	18
10.	Temperature Dependence of Thermoelectric Power (Germanium)	20
11.	Temperature Dependence of Thermoelectric Power (Lead Telluride)	23
12.	Temperature Dependence of Thermoelectric Power (Bismuth Telluride)	25
13.	Temperature Dependence of Thermoelectric Power (Bismuth Telluride)	28
14.	Seebeck Voltage versus Temperature (Lead Telluride)	34
15.	Resistivity versus Temperature (Lead Telluride)	35
16.	Photograph of Experimental Apparatus	42
17.	Photograph of Specimen Holder	43

1. Introduction.

When two dissimilar metals are connected in a closed loop and the two junctions maintained at different temperatures, several phenomena occur simultaneously. They are: (1) Seebeck Effect, (2) Joule Effect, (3) Peltier Effect, (4) Thomson Effect, and (5) the conduction of heat.

Considering each independently for the moment:

(1) Seebeck Effect - An electric current results from heating the junction of two dissimilar metals, and therefore a thermal emf exists between the two junctions. If the circuit is broken while maintaining the original temperatures of the junctions, the thermal emf is not altered.

(2) Joule Effect - The portion of the power input to any device which is equal to the product of the resistance of the conductors and square of the current is always converted to heat; that is, when a current I flows through a resistance R, heat is always dissipated in this resistance, and the rate of dissipation is $P_h = RI^2$.

(3) Peltier Effect - An electric current passing through a junction of dissimilar metals gives rise to a reversible heating or cooling effect, which is superimposed on the more usually observed Joule resistance heating effect. Extensive measurements have yielded the following [15]:[1]

(a) The rate at which the Peltier heat is transferred is proportional to the first power of the current (πI).

(b) Peltier heat is reversible, i. e., when the direction

[1]Numbers in brackets are bibliography references.

of the current is reversed, the magnitude remaining the same, the Peltier heat is the same but in the opposite direction.

(c) Peltier coefficient depends on the temperature and the materials of a junction being independent of the temperature of the other junction.

(4) Thomson Effect - A reversible heating or cooling effect exists within a homogeneous conductor in which there is a temperature gradient and an electric current. Measurements have yielded the follcwing:

(a) The rate at which the Thomson heat is transferred into a small region of a wire carrying a current, I, and supporting a temperature difference, dT, is equal to σ IdT where σ is the Thomson coefficient.

(b) The Thomson heat is reversible.

(c) The Thomson coefficient depends on the material of the wire and on the mean temperature of the small region under consideration.

(5) Conduction of Heat - Heat conduction is the transfer of heat energy in a single material by virtue of a temperature gradient. Actually, because this loop of two dissimilar materials is placed in an environment, there is a fin effect. That is, both conduction along the materials and convection to the environment exists. If, then, we assume a short insulated loop, the convection can be reduced to a negligible effect. The rate of conduction of heat is expressed by the Fourier relation, $\frac{q}{A} = -k\left(\frac{dt}{dx}\right)$.

The thermoelectric power, $\bar{a}$, which is defined as the rate of change of thermal emf with temperature, is perhaps one of the most

important properties in thermoelectric effects: $\bar{a} = \frac{dE}{dT}$.

The thermodynamic expressions relating the thermoelectric effects were conceived by Thomson (Lord Kelvin) and are now known as the Kelvin Relations. Using subscripts 1 and 2 to denote different substances, they are as follows:

$$\Pi_{12} = T \frac{dE_{12}}{dT} = T \bar{a}_{12} \tag{1}$$

$$\sigma_1 - \sigma_2 = T \frac{dE_{12}}{dT^2} \tag{2}$$

Π is the Peltier coefficient having dimensions of energy per unit charge. σ is the Thomson coefficient having the dimensions of electrical potential per degree. $\bar{a}_{12}$ can be recognized as a measure of the entropy difference per unit charge between substances, i. e., $\bar{a}_{12} = \bar{a}_1 - \bar{a}_2$, where $\bar{a}_1$ and $\bar{a}_2$ are the absolute thermoelectric powers of the substances 1 and 2 respectively. The thermoelectric power may also be defined by (2) as:

$$\frac{dE}{dT} = \int_0^T \sigma \frac{dT}{T}$$

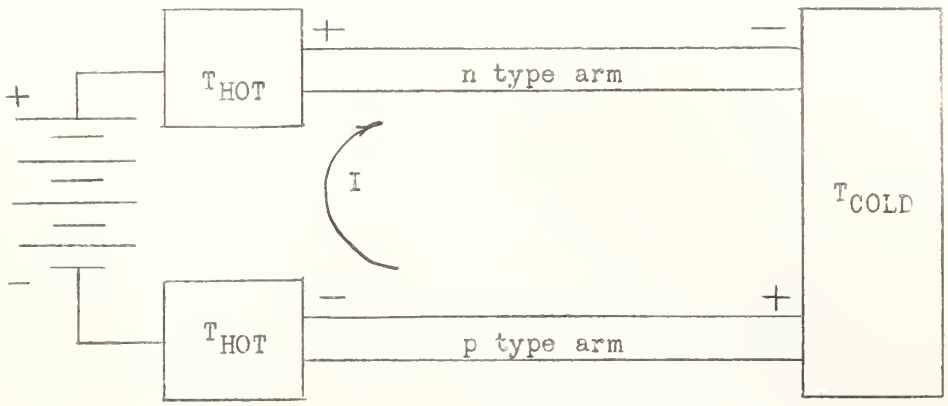
The utilization of semiconductors as thermoelectric materials has had a profound influence on the interest and development of the field of thermoelectricity. The thermoelectric power for semiconductor materials is an order of magnitude greater than for metals. Semiconductor materials possess still another thermoelectric advantage not found in metals. In some types of semiconductor materials, the electric poten-

tial established between the hot and cold junction is set up by the flow of negatively charged electrons; as a result, the cold end becomes negatively charged. In some other types, the electric potential established may be visualized as set up by the flow of positively charged "holes" vacated by electrons, and therefore the cold end becomes positively charged. This unique characteristic enables the thermoelectric power for each of two materials, which are called n and p respectively, to produce an additive effect when combined into a thermoelectric device (see Figure 1, noting polarity of the thermoelectric arms).

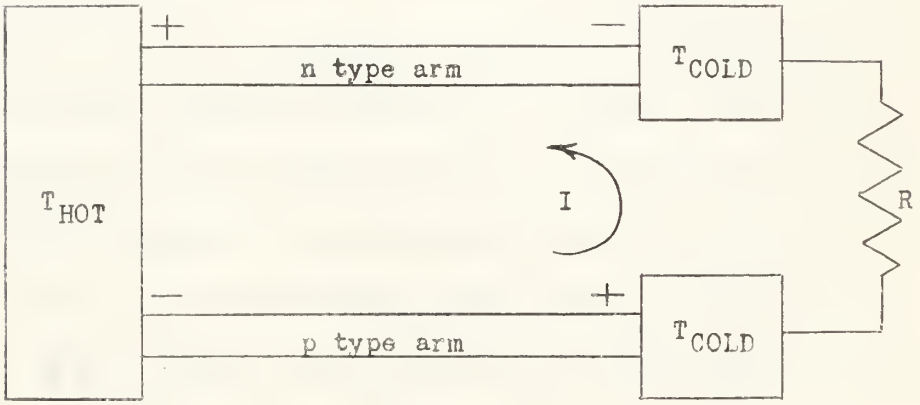
The practical application of thermoelectric effects is, to a large extent, a material problem, and it is desirable to have an index which characterizes the potential of various materials. Such an index is the figure of merit, z, which is a function of the thermoelectric power, the thermal conductivity, k, and the electrical resistivity, ρ, as follows: $Z = \frac{\overline{a}^2}{k\rho}$.

A thermoelectric device is fundamentally a heat engine and is governed by all the laws of thermodynamics as are other more well known heat engines.

The Carnot cycle efficiency is the maximum efficiency that any thermoelectric device can achieve operating between two fixed temperature limits. Since all the material parameters of the figure of merit, Z, can vary with temperature, certain materials may possess an optimum figure of merit at high temperatures and others an optimum figure of merit at lower temperatures. This implies that some materials will be more effective as thermoelectric generators and other materials



THERMOELECTRIC REFRIGERATOR



THERMOELECTRIC GENERATOR

Figure 1

more effective as thermoelectric refrigerators.

The thermoelectric power, the resistivity, and the thermal conductivity are not independent of each other, in fact, they are all functions of the concentration of the current carriers in the material. This can be denoted as N, and it can indicate either the number of negative carriers or positive carriers. The thermoelectric power tends to zero when N gets very large, and the thermoelectric power gets very large when N tends to zero. The thermal conductivity is the sum of two components, the lattice thermal conductivity and the electron thermal conductivity. Of course, the electron portion is again proportional to this carrier concentration. The ratio, thermoelectric power squared divided by resistivity, is a maximum at N in the order of 10^{19} carriers per cubic centimeter according to simplified theory [9]. The well known figure which encompasses insulators, semiconductors, and metals on the same diagram is presented in Figure 2. One would conclude from this discussion that semimetals or semiconductors would be the most likely candidates for promising materials, that is, it is a compromise between the thermoelectric power tending to large values at low carrier concentrations and the electrical conductivity tending to large values at high carrier concentrations.

The figure of merit can also be expressed: $Z = \bar{a}^2 \frac{\gamma}{k}$,

where γ represents electrical conductivity. This illustrates the need for an optimum ratio of electrical conductivity to thermal conductivity. The thermal conductivity is the sum of electron conductivity and lattice conductivity. In pure materials or perfectly homogeneous materials, the minimum thermal conductivity is represented by the

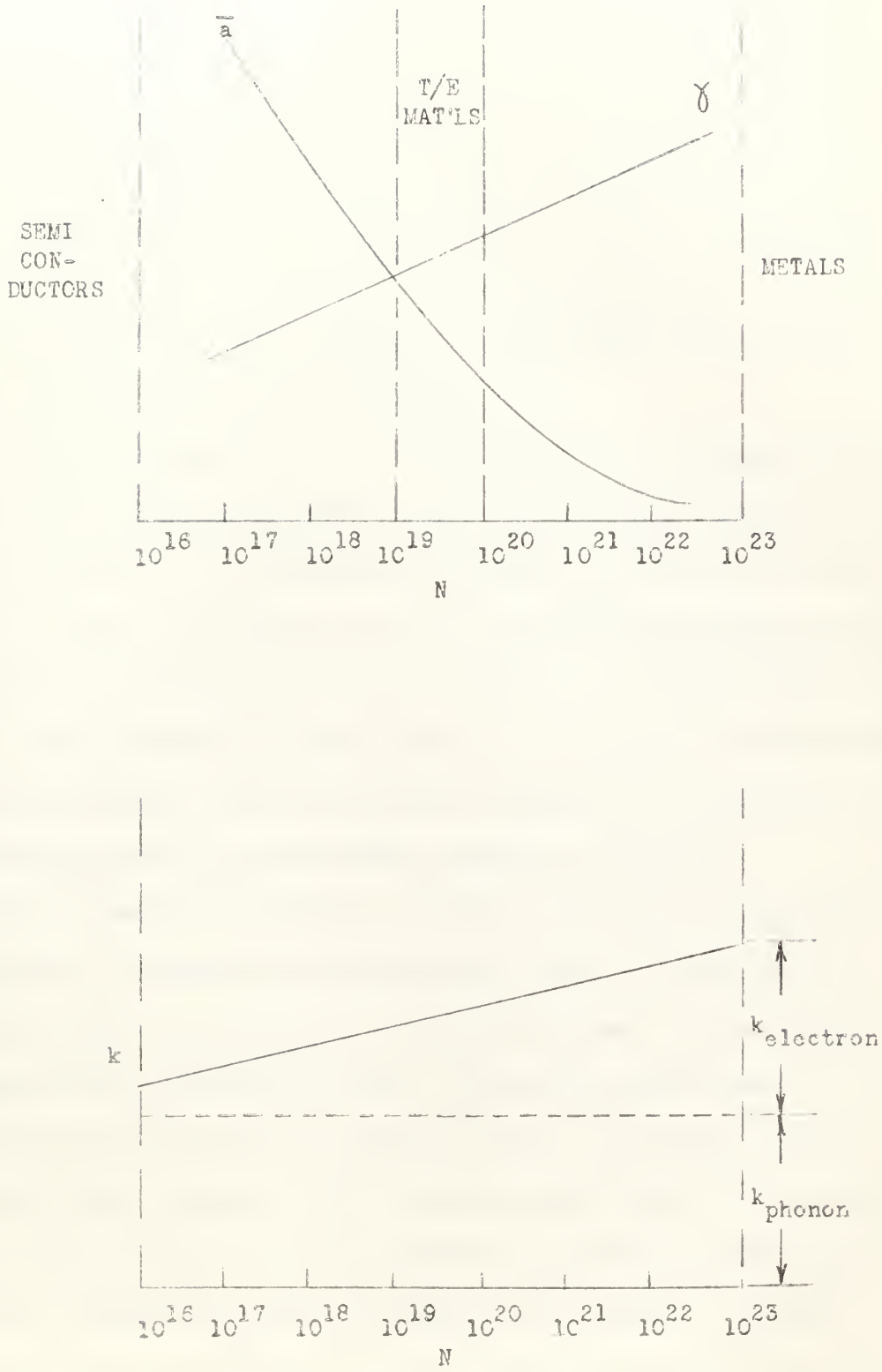


Figure 2. FIGURE OF MERIT PARAMETERS VERSUS CARRIER CONCENTRATION

lattice contribution. This is obtainable, however, only with zero charge carriers which would mean zero electrical conductivity. In order to have the maximum ratio of electrical conductivity to thermal conductivity, a material needs relatively few carriers and very high mobilities plus a low lattice conductivity. Mobility can be thought of as the ease in which the carriers travel in the material. High mobilities have been obtained in intermetallic compounds of medium atomic weight elements such as indium antimonide.

Introducing impurities into the material is the principal method available to alter the thermoelectric power, the resistivity, and the thermal conductivity in the desired direction. Impurities not only increase carrier concentration but may also decrease mobility so that the electrical conductivity cannot be regarded as strictly proportional to N. These impurities not only lead to an increase of the electronic portion of thermal conductivity and an increase of γ but also to a simultaneous decrease of the phonon thermal conductivity.

Then it should be possible to improve the ratio of electrical conductivity to thermal conductivity even further by reducing the lattice thermal conductivity. Ioffe [9] discusses the possibility of introducing into the lattice another substance, either element or compound, which crystallizes in a similar lattice and has approximately the same lattice constant. Such a system should exhibit fairly extensive solid solubility. Then the distortion of the basic lattice by the added impurity is relatively small and is limited to crystal regions in direct contact with impurity atoms. These distortions are effective in scattering thermal oscillations and as a result, the lattice thermal conductivity is appreciably reduced, but the current-carrying

mobility is not affected significantly because lattice periodicy is not altered. Thus, the electron waves with their longer lengths are not scattered effectively [10].

From the above discussion, it would appear that there is a good guide to selecting thermoelectric materials, i. e., in a desirable thermoelectric material it is necessary to have a high thermoelectric power, a high electrical conductivity, and a low thermal conductivity, or a high figure of merit. The difficulty here is that there are so many possibilities and nearly every possibility involves several elements. This leads to a great number of combinations, and the probability of getting or selecting an optimum combination by a trial and error procedure is out of the question. Thus, a more detailed method of selecting combinations from a theoretical approach coupled with experimental research is necessary.

As part of this continuing research program, H. P. R. Frederikse and T. H. Geballe, working independently [5, 7], observed an unusual rise in the thermoelectric power of single crystal germanium specimens (see Figure 3). Both observed this significant increase of thermoelectric power at low temperatures ($14^{\circ}K$ - $200^{\circ}K$). An analogous rise has been noted similar to the above for a number of other semiconductors, sometimes even more spectacular. Such is the case of p silicon, where thermoelectric powers up to 59 millivolts per degree have been reported [6].

The explanation given independently by Frederikse and Herring is that the additional thermoelectric power is caused by a drag exerted on the carriers by the phonon (lattice vibrational wave) which travels preferentially from hot to cold in a thermal gradient. This drag augments existing effects to give increased thermoelectric powers, and

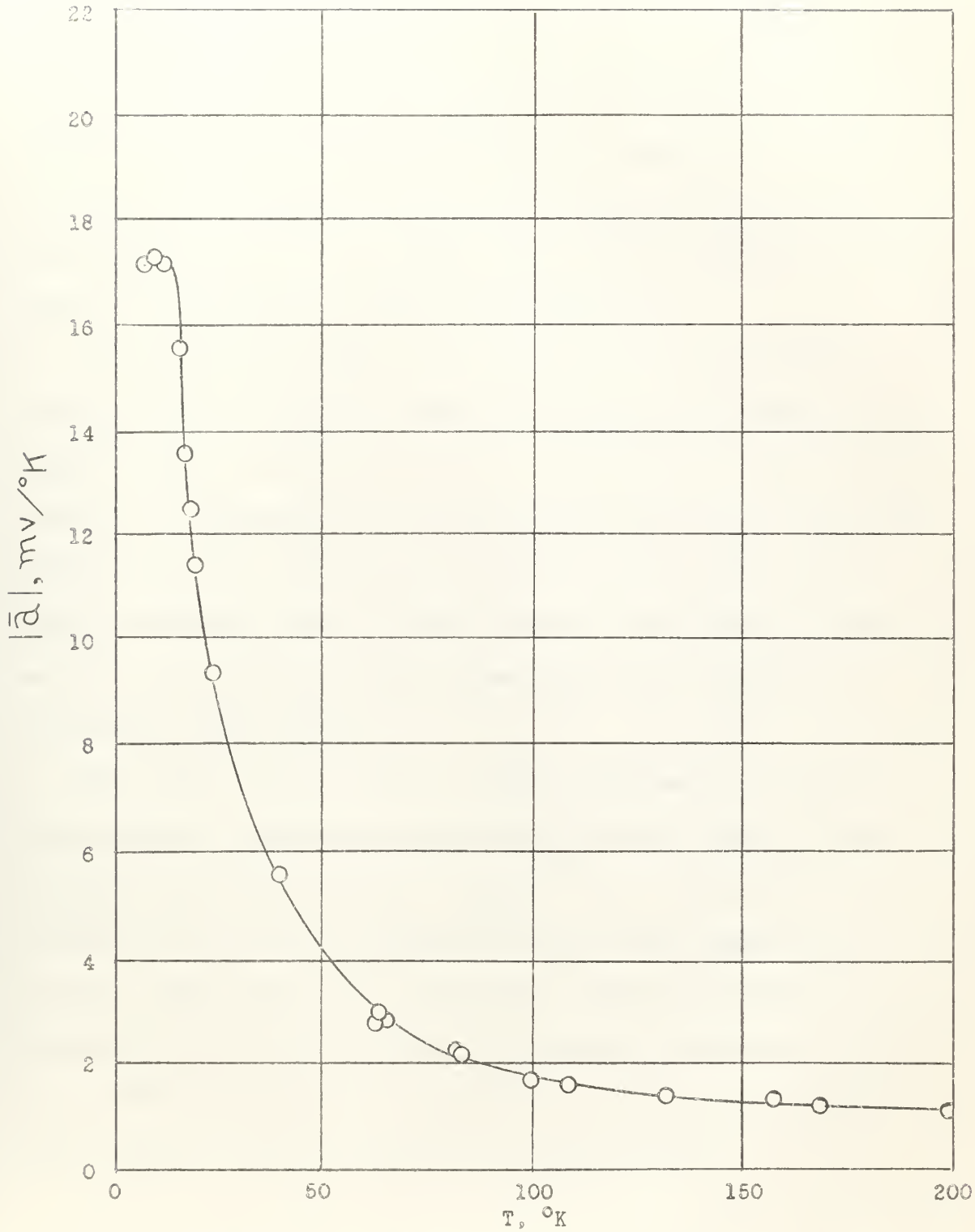


Figure 3. THERMOELECTRIC POWER OF GERMANIUM MEASURED FOR A 4 MM X 4 MM CROSS SECTION SAMPLE [8].

has been termed "phonon drag". The magnitude of the effect is therefore suspected to be a function of the carrier concentration. In a material possessing a high carrier density, the phonon drag will probably be small since any dragging along of carriers will be small in percentage to those already traveling in the substance. An optimum condition probably exists where the phonon drag contribution will be significantly large. It is worthy to note here that this phonon drag effect will be additive in both p and n materials.

Other investigators [2, 3, 14] , however, have reported no such appreciable phonon drag effect in germanium. The nature of their experiments was to determine the drift mobility of the carriers in the presence of a temperature gradient and to determine if any appreciable interaction between electrons and phonons can exist. These authors concluded that this interaction would always be negligible and that any rise in thermoelectric power at low temperatures could not be attributed to these effects.

Since the existence of such an effect might well be utilized in certain specific applications and certainly would advance the understanding of these interactions, it appears that a verification of this phenomenon of a rise in thermoelectric power at low temperatures is in order. This investigation attempts to satisfy this objective by measuring the thermoelectric power of germanium in the temperature range of 80°K to 230°K and to investigate this effect in two additional materials, lead telluride and bismuth telluride.

2. Analysis of problem and experimental techniques.

Figure 4 is a schematic diagram of the measurement of thermoelectric power. The measurement of thermoelectric power of one material with respect to another requires the establishment of a temperature gradient between two junctions and the measurement of the voltage developed between the two junctions. Ideally, the thermoelectric power, $\bar{a}$, is obtained from the ratio $\frac{\Delta E}{\Delta T}$ for $\Delta T \rightarrow 0$. In practice, $\bar{a}$ is found as a function of temperature by using ΔT values as small as the accuracy of the apparatus will permit.

The following considerations are essential for the design of a suitable apparatus:

(1) The specimen and associated equipment should be placed in a vacuum in order to minimize the temperature gradients caused by convection currents at the surface of the specimen. This also insures that the thermocouples are in thermal contact with the sample.

(2) Electrical leads to the sample and thermocouples should be small to reduce the errors due to thermal conduction.

(3) Heaters are necessary to maintain or establish the desired temperature gradient.

(4) The method of temperature measurement must be considered. In the temperature range of $100^{\circ}K$ - $230^{\circ}K$, thermocouples perform satisfactorily, and if copper-constantan thermocouples are used, the copper leg of each couple can also be utilized as the voltage probe for the measurement of the thermal emf of the specimen.

Figure 5 illustrates a common arrangement employed for the measurement of a thermal emf. A and B are the heat source and heat sink, respectively. C is the specimen being measured, and D and E are the

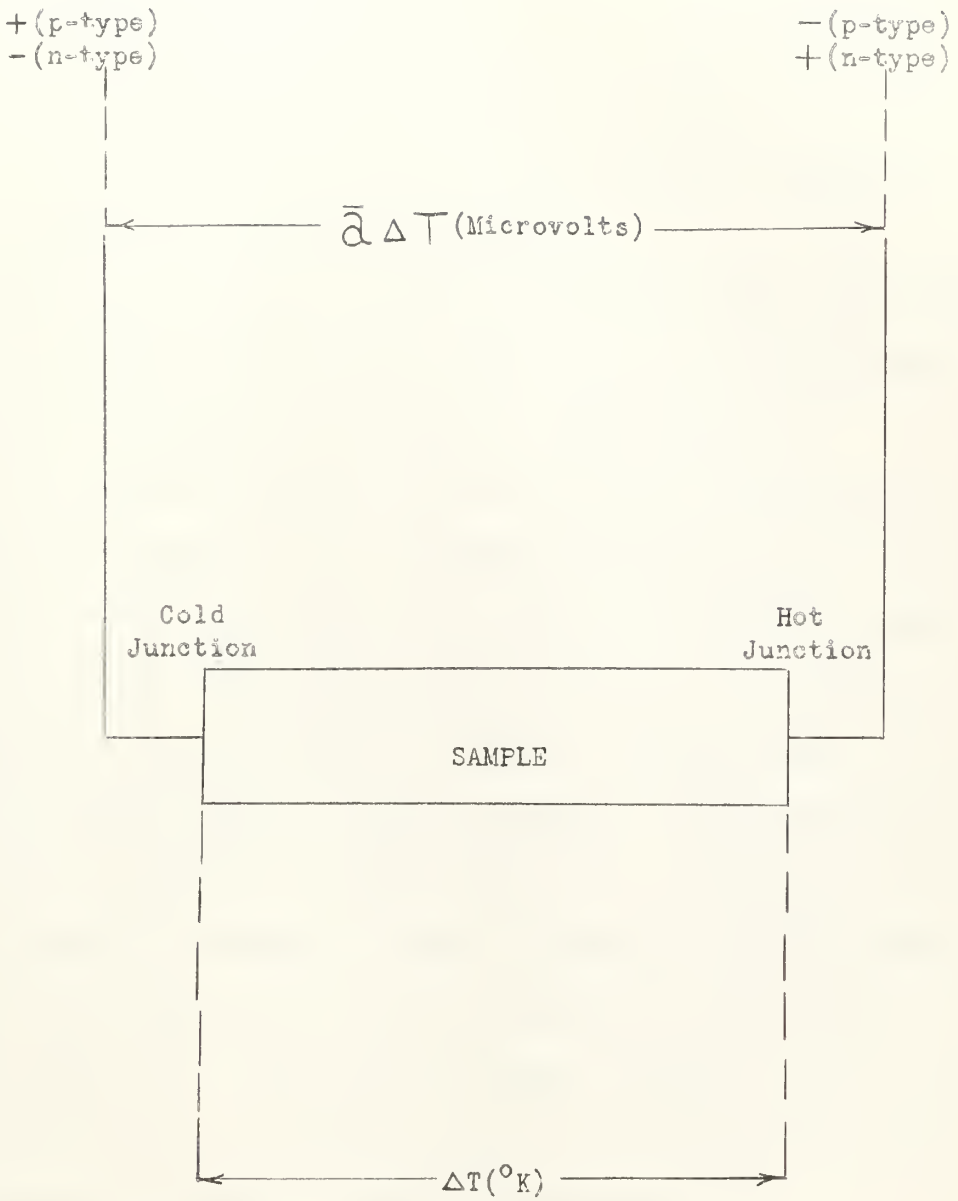


Figure 4. SCHEMATIC DIAGRAM OF THE MEASUREMENT OF THERMOELECTRIC POWER.

thermocouples. The thermoelectric power is then calculated from the relation $\bar{a} = \frac{\Delta E}{\Delta T}$. This method suffers a serious defect. Since a temperature gradient always exists between the specimen and the heat sinks, this temperature difference is proportional to the heat flux and thermal resistance of the contacts. As a result, the ΔT measured is higher than the true one, and the relation $\bar{a} = \frac{\Delta E}{\Delta T}$ gives too low a value for the thermoelectric power.

The error is reduced by mounting the thermocouples on the side of the specimen as illustrated in Figure 6, and is almost completely eliminated by removing the contacts as shown in Figure 7.

The apparatus designed and utilized in this investigation is illustrated in Figure 8. The specimen was mounted on two thin corrosion resistant steel strips, which acted as the heat path to the heat sink and heat source. The specimen was held firmly to the corrosion resistant steel strips by means of a plastic clamping device. The specimen was electrically insulated from the holder by a thin sheet of mica. The container was fabricated from pyrex glass. Housed in this container was an assembly consisting of heater A, heater B, and the specimen holder. The heaters were wound from nichrome wire onto brass cylinders. The wire was electrically insulated from the cylinder by means of a low temperature insulating varnish (GE # 7031). Each heater was approximately 100 ohms of electrical resistance.

The Seebeck Effect was measured in the steady state configuration. In order to maintain the desired temperature gradient between the junctions, heat was introduced at Heater 1, causing a drift in the sample temperature. This drift was followed until a steady state condition was reached. The thermocouple voltages and the thermal emf

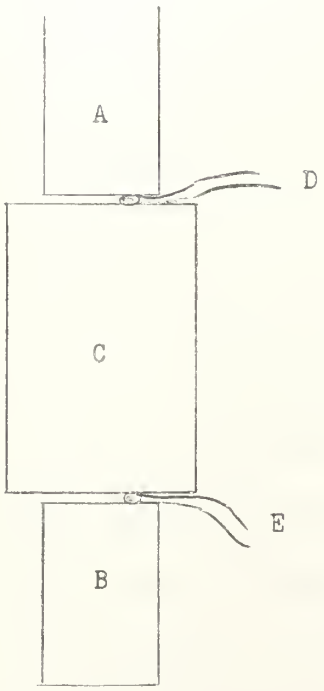


Figure 5.

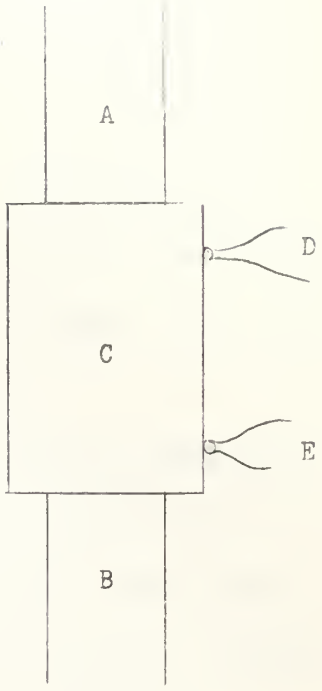


Figure 6.

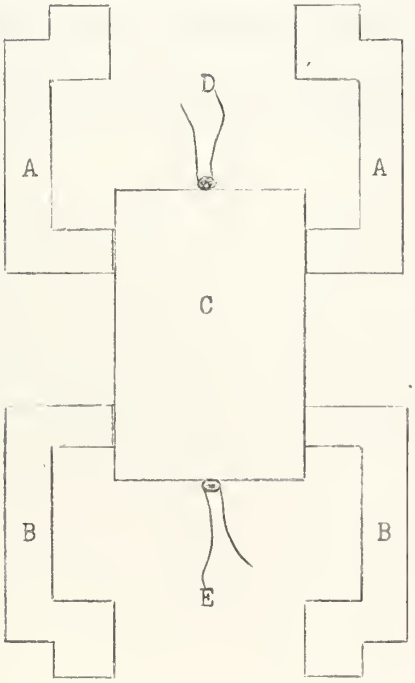


Figure 7.

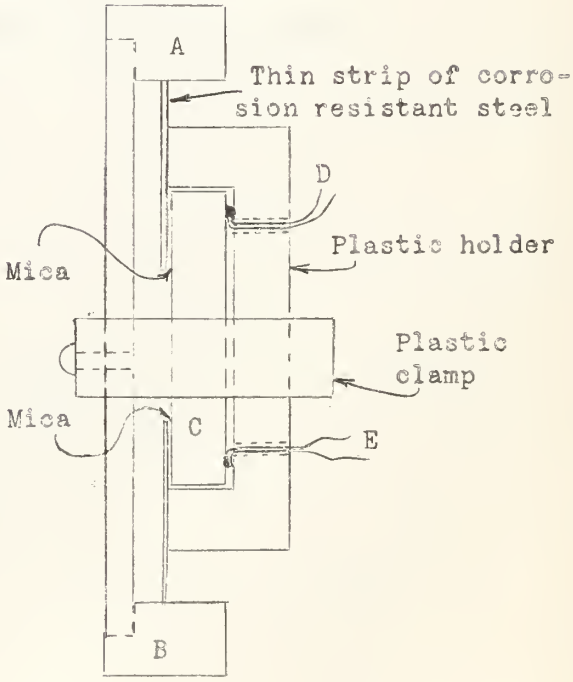


Figure 8.

were measured by means of a Rubicon potentiometer and a high sensitivity galvanometer. Parasitic emf's introduced by the rotation of the potentiometer drum were allowed to decay before taking measurements.

The following tests were performed before commencing a run:

(1) A drastic change was made in the container temperature without changing the specimen temperature. This showed that thermal conduction losses were not affecting the results.

(2) With the container having less than one micron of residual pressure, air was admitted at atmospheric pressure and the indicated specimen temperature was observed. A slight rise in the specimen temperature or no rise in the specimen temperature assured good thermal contact between the thermocouples and specimen.

After performing (1) and (2) above, the container was evacuated to not more than one micron of pressure to ready the apparatus for taking data. The temperature gradient between the junctions was maintained constant throughout a run.

3. Results

The thermoelectric power was found from the relation $\bar{a} = \frac{\Delta E}{\Delta T}$, where ΔE represents the thermal emf produced in the sample-copper circuit by the temperature difference ΔT between the junctions, where ΔT equals $T_1 - T_2$. The switching arrangement indicated in Figure 9 permitted the direct potentiometer reading of the emf, ΔE. It also allowed the measurement of the thermocouple emf for points one and two respectively. From the measured values of thermocouple emf E_1 and thermocouple emf E_2, together with the National Bureau of Standards' calibration data for copper-constantan thermocouples, the following was obtained: $T_a = \frac{T_1 + T_2}{2}$ and also $\left|\frac{dE}{dT}\right|_{T_a}$, where T_a is the average temperature and $\left|\frac{dE}{dT}\right|_{T_a}$ is the thermocouple emf per degree, respectively. This permitted determination of the temperature difference, ΔT, by the relation:

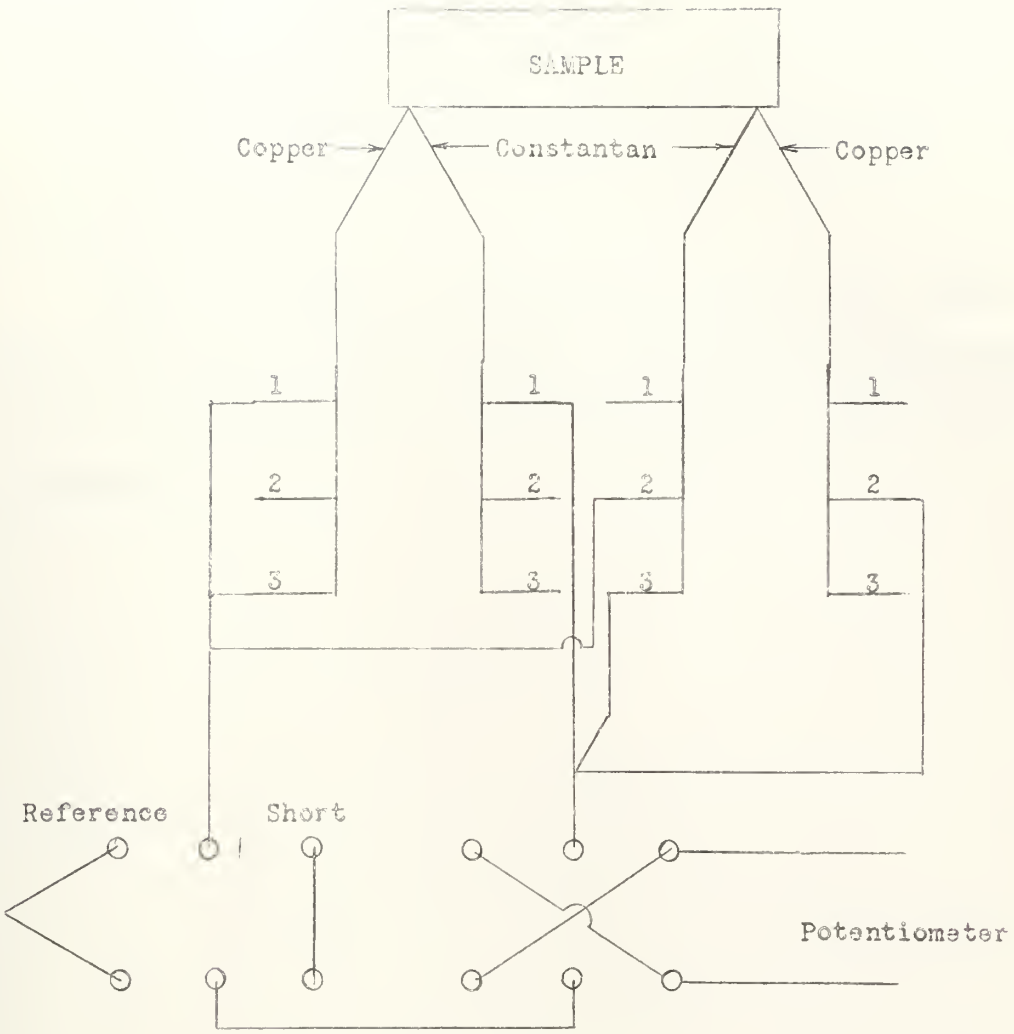
$$\Delta T = \frac{E_1 - E_2}{\left|\frac{dE}{dT}\right|_{T_a}}$$

Therefore, the thermoelectric power of the sample being measured at the temperature, T_a, was calculated from the equation,

$$\bar{a} = \left|\frac{dE}{dT}\right|_{T_a} \times \frac{\Delta E}{E_1 - E_2}$$

a value determined by three potentiometer readings, and the quantity $\left|\frac{dE}{dT}\right|_{T_a}$ taken from calibration tables.

Figure 10 presents the thermoelectric power versus temperature for a germanium specimen (see Appendix I for properties). There is



Reference position used when measuring thermocouple emf.
Short position used when measuring copper-sample emf.

Figure 9. SWITCHING ARRANGEMENT

no indication of a phonon drag effect in this specimen in the temperature range where measurements were performed.

Figure 11 presents the thermoelectric power versus temperature for the lead telluride specimen. This specimen does not exhibit any unusual increase in thermoelectric power in the temperature range reported.

Figure 12 presents the thermoelectric power versus temperature for the bismuth telluride specimen. This specimen yielded negative results also concerning a rise of thermoelectric power at these temperatures.

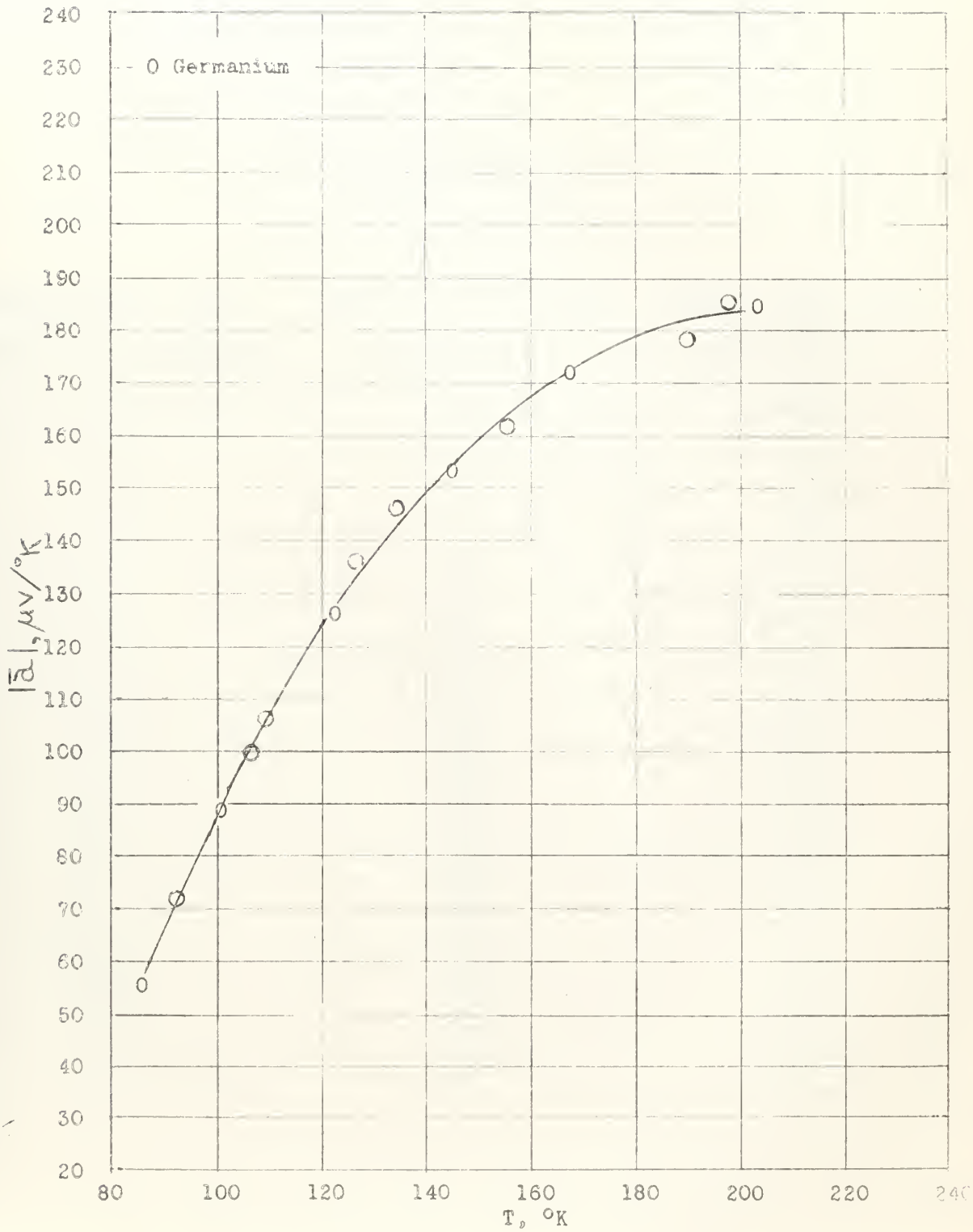


Figure 10. TEMPERATURE DEPENDENCE OF THERMOELECTRIC POWER

TABULATED RESULTS
GERMANIUM SAMPLE
RUN 1

THERMOELECTRIC POWER $\bar{a}$ MICROVOLTS PER DEGREE	TEMPERATURE DIFFERENCE ΔT DEGREES KELVIN	AVERAGE TEMPERATURE T_a DEGREES KELVIN
57.0	.806	85.95
72.0	.784	89.80
89.9	.737	99.60
100.0	.718	104.60
108.9	.739	109.47
127.9	.694	121.62
139.9	.655	129.76
147.9	.678	136.7
156.9	.720	146.21
161.9	.798	154.61
174.9	.810	169.69
179.9	.798	184.59
184.9	.797	199.64
186.9	.797	207.60

TABULATED RESULTS
GERMANIUM SAMPLE
RUN 2

THERMOELECTRIC POWER $\bar{a}$ MICROVOLTS PER DEGREE	TEMPERATURE DIFFERENCE T DEGREES KELVIN	AVERAGE TEMPERATURE T_a DEGREES KELVIN
60.	.78	82.4
68	.80	90.2
81	.81	94.6
110	.81	110.9
120	.83	114.5
127	.82	119.6
151	.84	140.1
155	.84	144.6
161	.84	149.5
175	.85	169.7
177	.84	174.5
179	.85	179.8

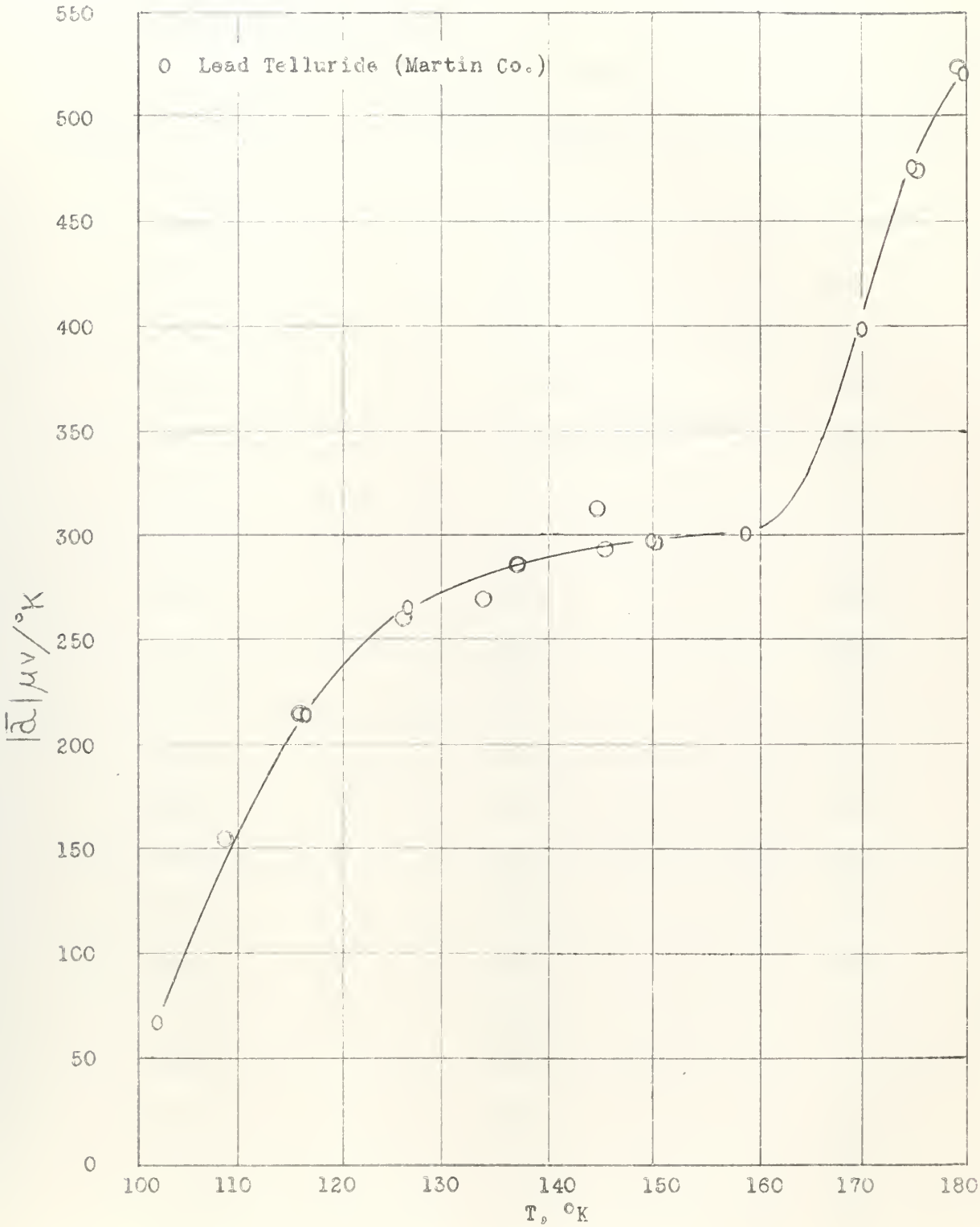


Figure 11. TEMPERATURE DEPENDENCE OF THERMOELECTRIC POWER

TABULATED RESULTS
LEAD TELLURIDE "N" TYPE

THERMOELECTRIC POWER $\bar{a}$ MICROVOLTS PER DEGREE	TEMPERATURE DIFFERENCE ΔT DEGREES KELVIN	AVERAGE TEMPERATURE T_a DEGREES KELVIN
-63.7	.259	102.1
-72.5	.212	102.0
-159.6	.249	107.9
-215.2	.261	116.9
-262.1	.354	127.0
-259.9	.407	128.7
-256.8	.508	135.6
-269.8	.577	137.7
-250.9	.611	142.3
-316.1	.498	145.4
-309.5	.514	146.0
-285.1	.578	147.8
-294.1	.575	150.2
-295.0	.571	150.6
-299.9	.571	159.8
-399.8	.556	169.9
-474.9	.596	176.7
-469.8	.627	177.7
-519.8	.619	180.1
-543.8	.619	181.6
-589.8	.597	184.7

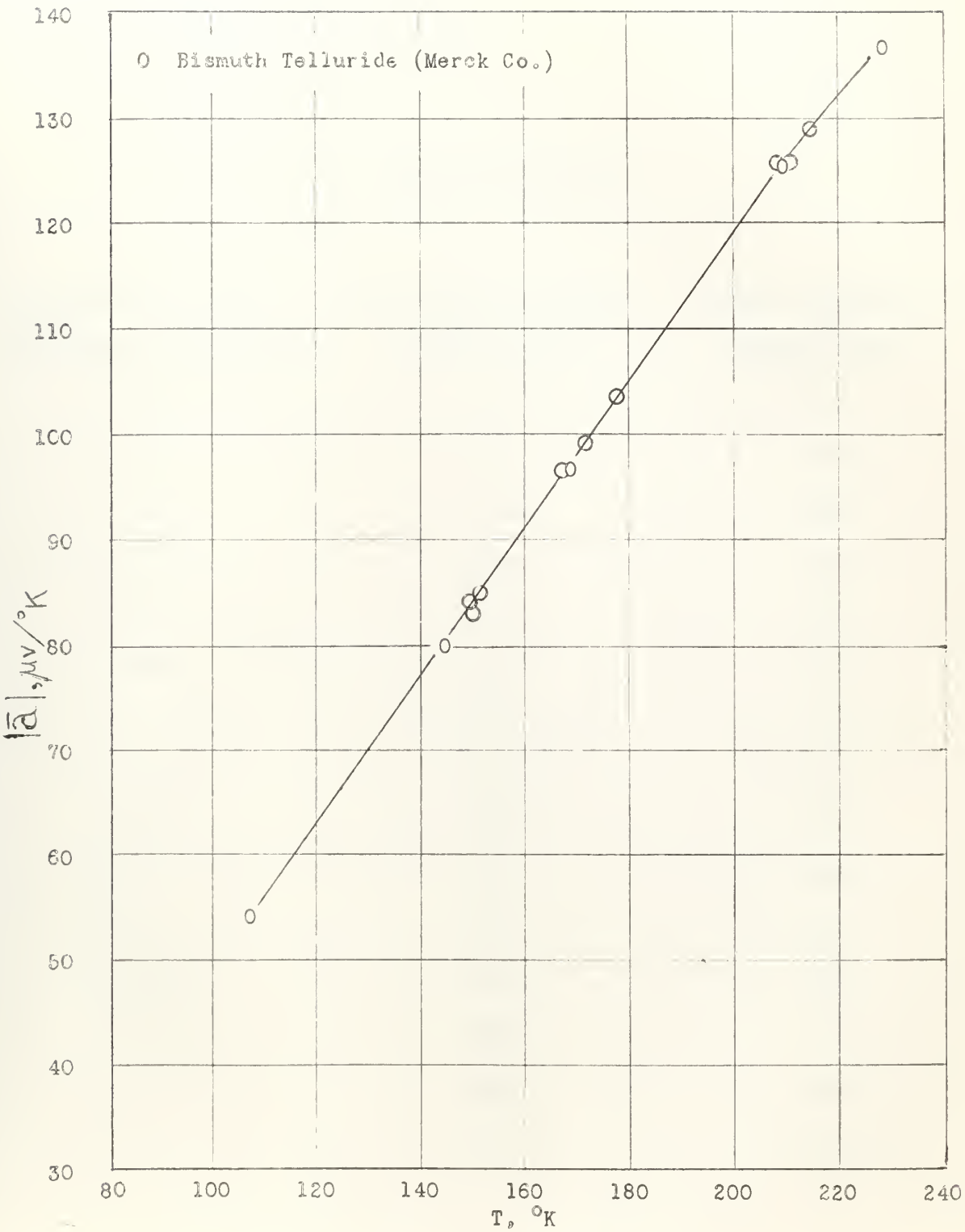


Figure 12. TEMPERATURE DEPENDENCE OF THERMOELECTRIC POWER

TABULATED RESULTS
BISMUTH TELLURIDE "P"

THERMOELECTRIC POWER $\bar{a}$ MICROVOLTS PER DEGREE	TEMPERATURE DIFFERENCE ΔT DEGREES KELVIN	AVERAGE TEMPERATURE T_a DEGREES KELVIN
53.9	1.00	107.3
80.1	1.98	143.5
84.8	1.73	149.8
81.2	1.81	151.3
86.8	1.73	157.3
90.9	1.71	157.3
98.0	1.76	163.0
96.5	1.75	168.6
99.9	1.88	173.1
103.7	1.75	178.5
139.5	2.15	205.5
125.3	2.33	209.8
127.7	2.02	211.8
129.1	1.85	213.9
134.3	1.62	227.5

4. Conclusions.

For the samples measured, there does not seem to be any indication of a phonon drag effect. The writer does not believe that the nature of these results should rule out the fact that there is a phonon drag effect or that it can be appreciable in certain temperature ranges. The results emphasize the need for a detailed method of selecting material combinations and material properties coupled with experimental research in order that the most significant advances in the tailoring of thermoelectric material properties can be made.

In view of the dependence of thermoelectric power on carrier density and resistivity, specimens exhibiting a range of values of these parameters should be studied. For this experiment, measurements were limited to specimens most readily available.

The lead telluride specimen was fabricated by a pressed and sintered process. Any appreciable phonon drag effect seems to be limited to single crystal type specimens [13] and the results of measurements on this sample appears to support this expectation.

The bismuth telluride sample was obtained indirectly from the Merck Company, and its properties are not known. The method of fabrication is also unknown and therefore it can only be speculated that the sample is probably similar to the lead telluride sample and is a polycrystalline material which is not expected to exhibit any appreciable phonon drag effect. The results seem to be in qualitative agreement with other values reported [4] for other bismuth telluride type samples (see Figure 13).

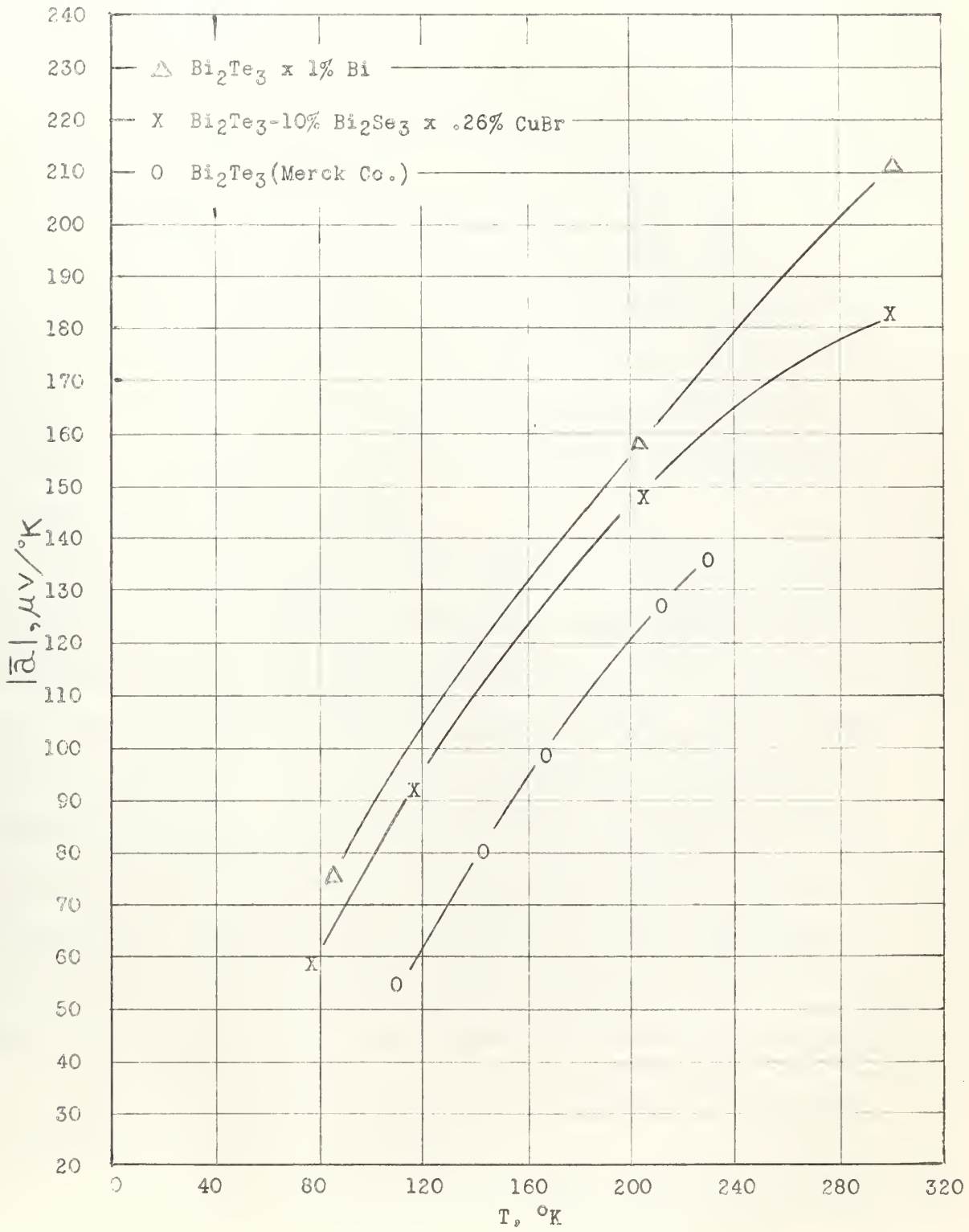


Figure 13. TEMPERATURE DEPENDENCE OF THERMOELECTRIC POWER

5. Recommendations concerning future work.

As a result of this investigation, it is recommended that additional measurements be performed on samples of compounds having properties which possess, as described earlier, a greater potential for exhibiting this phonon drag effect. These measurements should be performed at temperatures extending below those of this report. Temperatures down to the vicinity of 50°K would probably yield more conclusive results. Measurements in this temperature range can be accomplished without the necessity of introducing any of the hazards of liquid hydrogen. Utilizing a liquid helium refrigerant bath with the specimen container held above this bath, the above recommended temperature range could be achieved.

However, there is an additional difficulty introduced concerning the method of temperature measurement. Thermocouples of copper-constantan and/or chrome-alumel have been used by other workers [6, 7] in and below the temperature range of 50°K to 270°K. These couples, if used, would have to be accurately calibrated, since the National Bureau of Standards' calibration tables do not extend below 75°K for these materials. The Bureau of Standards will, however, calibrate thermocouples composed of these materials in the above temperature range when so requested. Thermocouples constructed of silver versus gold (+2% cobalt) are also recommended in this temperature range [11].

Some of the difficulties which need not plague an experimenter continuing this work are as follows:

(1) There is a thermocouple contact problem which involves keeping the thermocouple junction in excellent thermal contact with the specimen throughout the entire temperature range of interest.

This can be solved either by means of pressure contacts or by soldering the junction directly to the specimen utilizing an Indalloy Solder (Cerroseal) distributed by the Indium Corporation of America. The important factor is surface preparation prior to soldering which is accomplished by sand blasting or etching to give a clean surface. Careful attention so as not to contaminate the surface by touching will permit effecting a good bond.

(2) The problem of maintaining a vacuum of one micron or less with an all metal container exists. The container should be constructed to permit convenient access for changing specimens. A neoprene type O ring does not work satisfactorily in this temperature range. The solution can be effected by constructing the container to permit complete sealing by silver brazing or soldering which will accomplish an effective seal. An alternate method is to construct the container using pyrex glass, utilizing a ground glass joint for access. The former method was employed by Frederikse [5], the latter by the writer. Initially, significant temperature gradients could not be obtained in the vicinity of the refrigerant bath temperature. The lower heat sink could only lose its heat to the bath by radiation which required considerable time. To facilitate this heat transfer, a metal probe was placed through the lower portion of the container to provide a heat path from the sink to the refrigerant bath. This probe solved the problem satisfactorily.

(3) Difficulty was experienced by the writer in maintaining a substantial temperature gradient across the specimen. It is recommended before further work is attempted that samples of small cross-section and considerable length (two to three inches) be obtained.

This type of specimen would enable an experimenter to maintain an appreciable temperature gradient (perhaps several degrees) thereby increasing the accuracy of the measurement of the thermoelectric power.

(4) The leads for the thermocouples and the electric heaters have to be brought out through the system; if the container is metal, it is recommended that factory-prepared seals such as Kovar seals (available from the Carborundum Co.) be obtained for passing the thermocouples' leads through the container without introducing a new material in the thermocouple circuit. In the case of the glass container, an epoxy resin cement was found to work satisfactorily at the pressures required for sealing the electrical and thermocouple lead wires where they pass through the glass.

(5) The possibility of measuring temperature difference directly will intrigue any experimenter continuing this work. To accomplish this, it will be necessary to effect a good thermal contact between the thermocouple junction and the specimen, but at the same time, maintain electrical isolation between the two. This is necessary in order to eliminate any extraneous thermal emf's induced in the thermocouple-specimen circuit. Recently, in reference to a project performed by Geballe, Herring [13] cited that this had been accomplished. This should enhance the accuracy of these measurements even further.

BIBLIOGRAPHY

1. American Institute of Physics Symposium, Temperature, Its Measurement and Control in Science and Industry, New York, Reinhold Publishing Corp., 1941.

2. Baranskii, P. I., Mobility of Minority Charge Carriers in Coaxial Electrical and Thermal Fields, J. Tech. Phys., (USSR), 27, p. 221 (1957); 26, p. 683 (1956); 27, p. 233 (1957).

3. Baranskii, P. I. and V. E. Lashkarev, Measurement of the Bulk Thermal EMF in Germanium, Soviet Physics Technical Physics, Vol. 2, No. 6, pp. 1055-1060, June 1957.

4. Bate, R. T., Technical Report No. 3 on Thermoelectric Properties of Bi_2Te_3 - Bi_2Se_3 Alloys, to Chief, Physics Branch, Office of Naval Research, Columbus, 1960.

5. Frederikse, H. P. R., Thermoelectric Power of Germanium below Room Temperature, Physical Review, Vol. 92, No. 2, pp. 248-252, Oct. 15, 1953.

6. Geballe, T. H. and G. W. Hull, Seebeck Effect, Physical Review, 98, p. 940, 1955.

7. Geballe, T. H. and G. W. Hull, Seebeck Effect in Germanium, Physical Review, Vol. 94, No. 5, pp. 1134-1140. June 1, 1954.

8. Hannay, N. B., Semiconductors, New York, Reinhold Publishing Corp., 1959.

9. Ioffe, A. F., Semiconductor Thermoelements and Thermoelectric Cooling, London, 1957.

10. Jaumot, Frank E., Jr., Thermoelectric Effects, Institute of Radio Engineers Proceedings, Mar. 1958, 46 Pt. 1:538-554.

11. Marton, L., Methods of Experimental Physics, Volume 6 - Part B, Solid State Physics, New York, Academic Press Inc., 1959.

12. Middleton, A. E. and W. W. Scanlon, Measurement of the Thermoelectric Power of Germanium at Temperatures above 78°K, Physical Review, Vol. 92, No. 2, pp. 219-226, Oct. 15, 1953.

13. Semiconductors and Phosphors, New York, Interscience, 1958.

14. Shtenbeck, M. and P. I. Baranskii, The Motion of Minority Carriers in Germanium, Soviet Physics Technical Physics, Vol. 2, No. 2, pp. 195-204, Feb. 1957.

15. Zemansky, M. W., Heat and Thermodynamics, New York, 1957.

APPENDIX I

PROPERTIES OF SPECIMENS MEASURED

Germanium, P-type (parameters measured at 296.7°K):

Resistivity	1.540	ohm-cm
Mobility	298	$cm^2(volt\text{-}sec)^{-1}$
Carrier concentration	1.358×10^{16}	cm^{-3}
Dimensions	.160" x .160" x .890"	square rod

Bismuth telluride:

Dimensions	.182" x .200" x .819"	rectangular rod

Lead telluride:

Dimensions	.180" x .180" x .825"	square rod

Pressed and sintered samples, see Figures [14, 15] for Seebeck Voltage versus temperature and resistivity versus temperature.

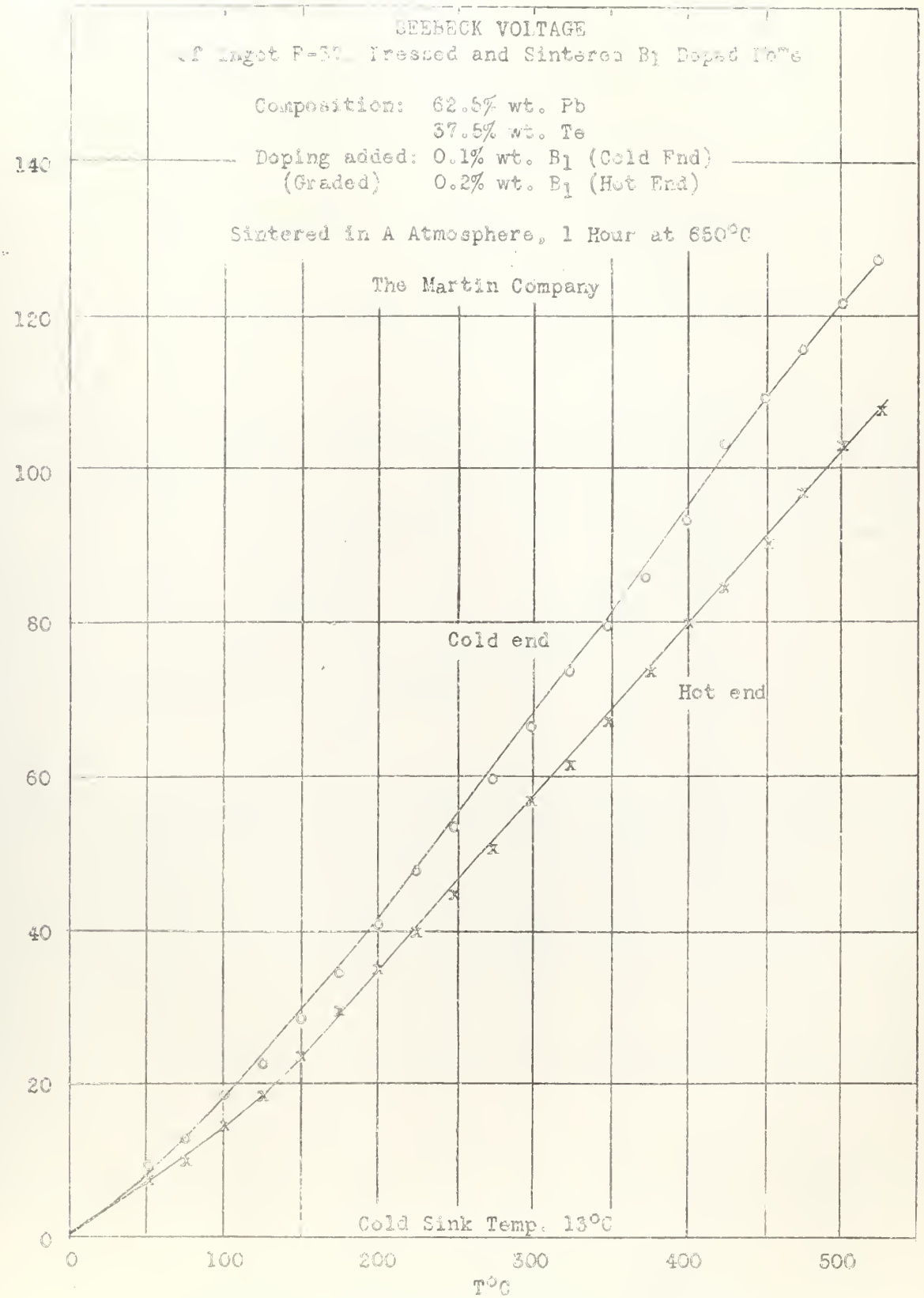


Figure 14. SEEBECK VOLTAGE VERSUS TEMPERATURE

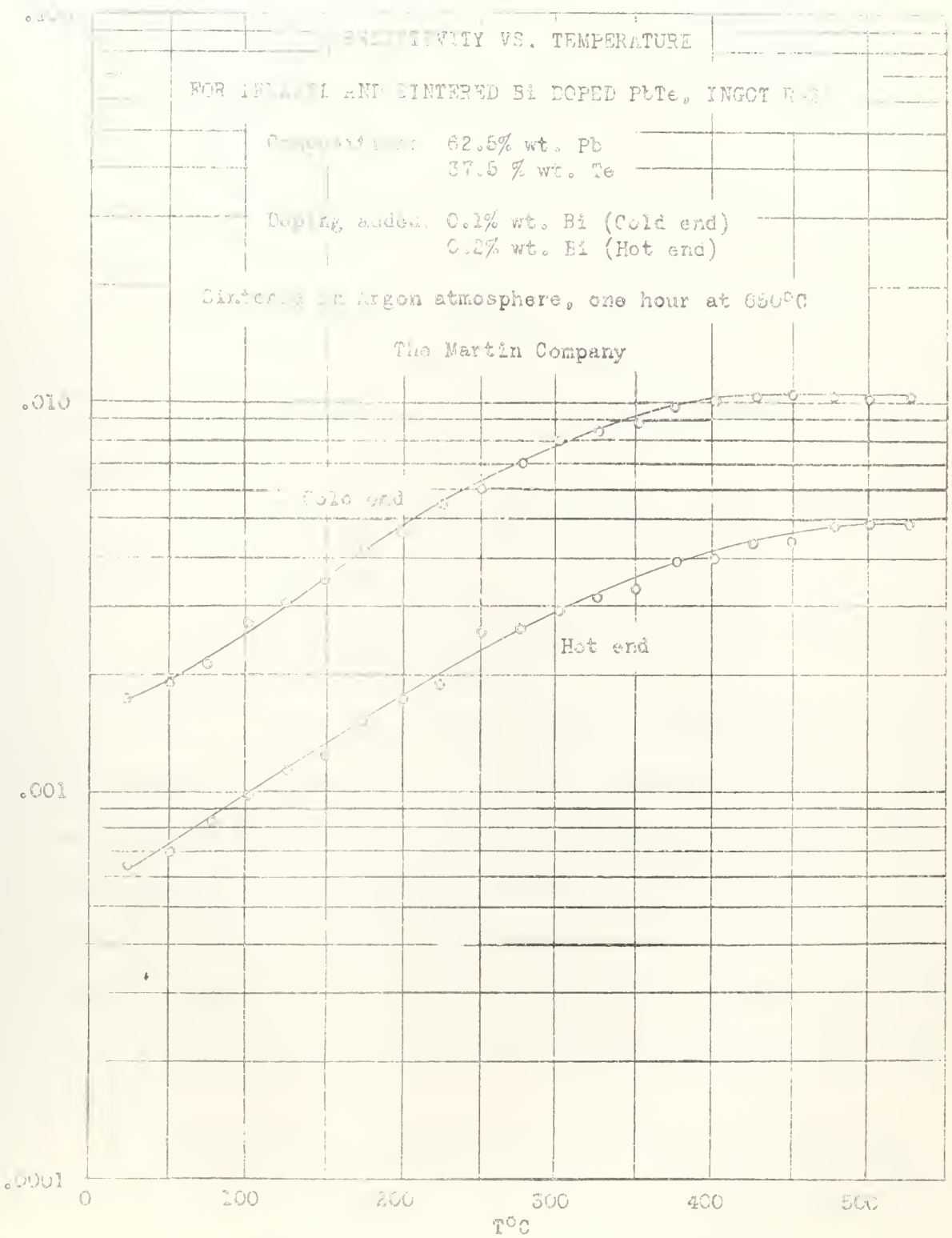


Figure [illegible] RESISTIVITY VERSUS TEMPERATURE

APPENDIX II

EXPERIMENTAL ERRORS

The principal source of error in the measurement of thermoelectric power, $\bar{a}$, occurred in the measurement of the difference in temperature between the points one and two on the surface of the sample. This difference was usually in the vicinity of one degree centigrade so that the temperature difference should be known to within 0.05 degrees centigrade to determine $\bar{a}$ to within five percent. Problems of precision thermometry with thermocouples[1] have indicated the following conditions must be met in measurements of surface temperatures:

(1) The thermocouples should not distort the established isotherms in the vicinity.

(2) The thermocouple wires should be uniform in composition and reproducible in calibration.

The pair of thermocouples used in this investigation was matched in an attempt to avoid errors due to non-uniformity of the wires. The two junctions placed in contact with the sample were formed from the same material and kept as nearly identical in size as possible. Since the use of fine wires may have introduced errors due to non-uniformity of the thermocouple wires and large wires would have made the heat loss by conduction significant, a compromise of size 30 thermocouple wire was selected.

Appreciable temperature gradients across the sample were difficult to obtain at low temperatures due to the high thermal conductivity of the sample. The smallest temperature difference between one and two measured was 0.2 degrees, for which the accuracy of the thermoelectric

power was estimated at ten percent.

APPENDIX III

GERMANIUM
EXPERIMENTAL DATA

THERMOCOUPLE READINGS E_1 MILLIVOLTS	E_2	SEEBECK EMF ΔE MILLIVOLTS	PRESSURE p MICRONS
RUN NO. 1:			
5.3340	5.3203	.0460	1
5.2621	5.2583	.0564	1
5.0823	5.0783	.0663	1
4.9909	4.9769	.0718	1
4.8951	4.8801	.0805	1
4.6397	4.6245	.0888	1
4.4577	4.4427	.0917	1
4.2965	4.2805	.1003	1
4.0666	4.0487	.1128	1
3.8544	3.8338	.1293	1
3.4508	3.4284	.1415	1
3.0262	3.0028	.1437	1
2.5715	2.5467	.1475	1
2.3191	2.2936	.1490	1
RUN NO. 2:			
5.3932	5.3802	.0472	1
5.2604	5.2463	.0544	1
5.1815	5.1668	.0654	1
4.8503	4.8668	.0894	1
4.7913	4.7741	.0992	1
4.6840	4.6663	.1040	1
4.2188	4.1986	.1265	1
4.1068	4.0862	.1297	1
3.9836	3.9622	.1356	1
3.4513	3.4278	.1488	1
3.3145	3.2908	.1489	1
3.1648	3.1403	.1515	1

APPENDIX III

LEAD TELLURIDE
EXPERIMENTAL DATA

THERMOCOUPLE READINGS E_1 MILLIVOLTS	E_2	SEEBECK EMF $\triangle E$ MILLIVOLTS	PRESSURE p MICRONS
5.0365	5.0315	.0165	1
5.0365	5.0324	.0154	1
4.9222	4.9172	.0397	1
4.7373	4.7318	.0561	1
4.4986	4.5068	.0951	1
4.4798	4.4906	.1058	1
4.3211	4.3091	.1306	1
4.2726	4.2588	.1558	1
4.1466	4.1615	.1532	1
4.0712	4.0836	.1574	1
4.0554	4.0682	.1591	1
4.0103	4.0248	.1647	1
3.9506	3.9652	.1693	1
3.9410	3.9555	.1696	1
3.7134	3.6982	.1714	1
3.4407	3.4253	.2223	1
3.2514	3.2343	.2830	1
3.2238	3.2058	.2947	1
3.1540	3.1371	.3220	1
3.1047	3.0967	.3364	1
3.0195	3.0020	.3523	1

APPENDIX III

BISMUTH TELLURIDE
EXPERIMENTAL DATA

THERMOCOUPLE READINGS E_1 MILLIVOLTS	E_2	SEEBECK EMF $\triangle E$ MILLIVOLTS	PRESSURE p MICRONS
4.9490	4.9292	.0539	1
4.1523	4.1040	.1587	1
3.9938	3.9503	.1471	1
3.9560	3.9100	.1470	1
3.8383	3.7938	.1520	1
3.7998	3.7552	.1553	1
3.6486	3.6015	.1722	1
3.4930	3.4449	.1687	1
3.4900	3.4382	.1883	1
3.1834	3.1327	.1833	1
2.4095	2.5415	.3003	1
2.2922	2.2275	.2929	1
2.2359	2.1708	.2582	1
2.1666	2.1065	.2395	1
1.6808	1.6258	.2174	1

APPENDIX IV

SAMPLE CALCULATIONS

GERMANIUM SPECIMEN

THERMOCOUPLE READINGS MILLIVOLTS		SEEBECK EMF MILLIVOLTS
E_1	E_2	ΔE
5.3340	5.3203	.0460

$$E_1 - E_2 = 0.0137 \text{ mv}$$

$$\frac{E_1 + E_2}{2} = 5.3271 \text{ mv}$$

At 5.3271 mv in Copper Constantan Thermocouple Calibration Tables,

$T_{AVERAGE} = -187.05^{\circ}C = 85.95^{\circ}K$

From calibration tables at $T_a = 85.95^{\circ}K$

$$\left(\frac{dE}{dT}\right)_{T_a} = .0169 \text{ mv/degree}$$

$$\therefore \quad \Delta T = \frac{E_1 - E_2}{\left(\frac{dE}{dT}\right)_{T_a}}$$

Then the thermoelectric power for germanium at $T_a = 85.95^{\circ}K$, is,

$$\bar{a} = \frac{\text{Seebeck emf}}{\Delta T^{\circ}K} = \frac{\text{Seebeck emf}}{\frac{E_1 - E_2}{\left(\frac{dE}{dT}\right)_{T_a}}} = \frac{.0460\ (.0169)}{.0137}$$

$$= .0567 \text{ mv}/^{\circ}K \longrightarrow 56.7 \text{ microvolts}/^{\circ}K$$

FIGURE 16 EXPERIMENTAL APPARATUS ARRANGEMENT

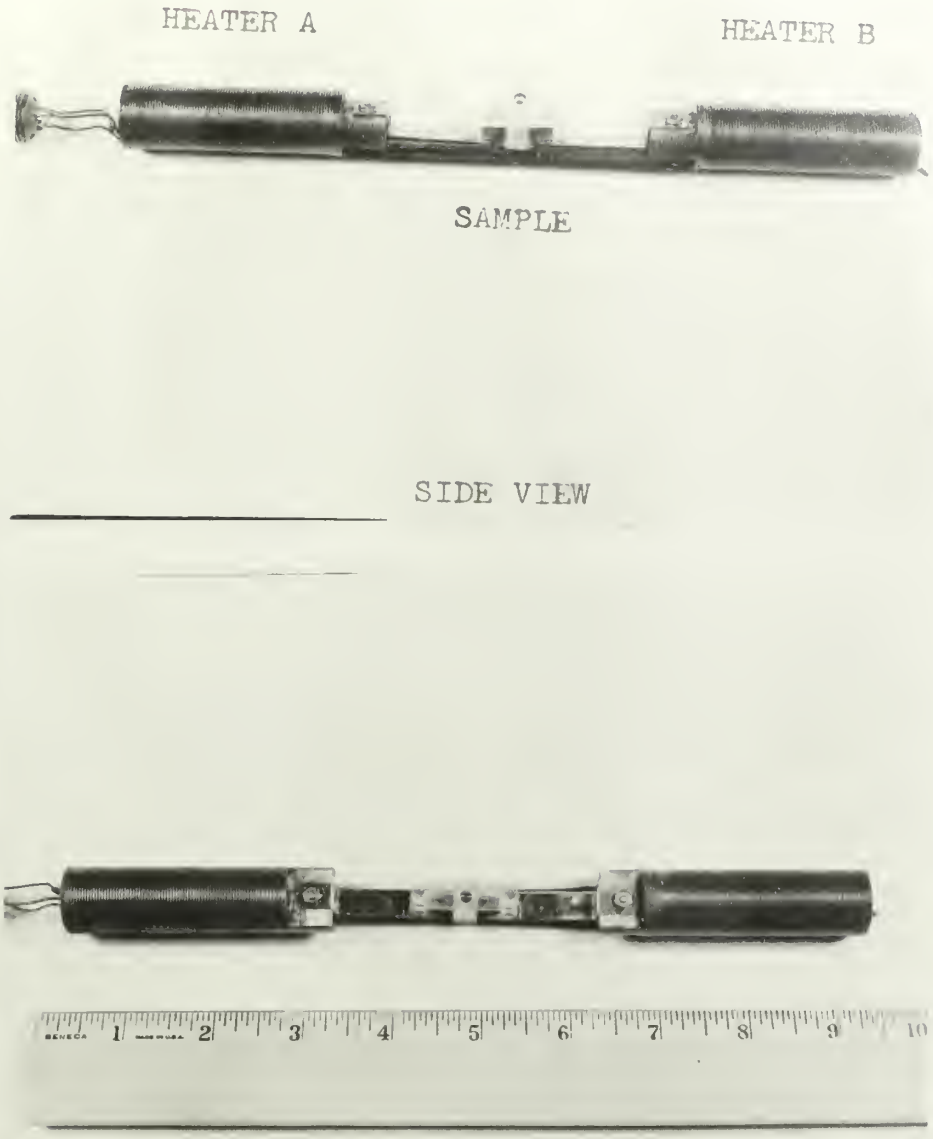


FIGURE 17 SPECIMEN HOLDER

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Measurement of thermoelectric power in t
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